

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
30 August 2001 (30.08.2001)

PCT

(10) International Publication Number
WO 01/62847 A1

(51) International Patent Classification⁷: C08L 23/04,
C08F 10/02, 297/08, B29C 47/02

(21) International Application Number: PCT/FI01/00161

(22) International Filing Date: 19 February 2001 (19.02.2001)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
20000397 21 February 2000 (21.02.2000) FI

(71) Applicant (for all designated States except US): BORE-
ALIS TECHNOLOGY OY [FI/FI]; P.O. Box 330, FIN-
06101 Porvoo (FI).

(72) Inventors; and

(75) Inventors/Applicants (for US only): VÄHÄLÄ, Martti
[FI/FI]; Tilanomistajantie 4 1, FIN-06400 Porvoo (FI).
SALMINEN, Hannu [FI/FI]; Ruohikkopolku 6 E 9,
FIN-06400 Porvoo (FI). LEHTINEN, Arja [FI/FI];
Fleminginkatu 4 A 9, FIN-00530 Helsinki (FI).

(74) Agent: SEppo LAINE OY; Itämerenkatu 3 B,
FIN-00180 Helsinki (FI).

(81) Designated States (national): AE, AG, AL, AM, AT, AT
(utility model), AU, AZ, BA, BB, BG, BR, BY, BZ, CA,
CH, CN, CR, CU, CZ, CZ (utility model), DE, DE (utility
model), DK, DK (utility model), DM, DZ, EE, EE (utility
model), ES, FI, FI (utility model), GB, GD, GE, GH, GM,
HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK,
LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX,
MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SK
(utility model), SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ,
VN, YU, ZA, ZW.

(84) Designated States (regional): ARIPO patent (GH, GM,
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian
patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European
patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE,
IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF,
CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:

- with international search report
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.



WO 01/62847 A1

(54) Title: PROCESS FOR PRODUCING A POLYETHYLENE COATING ON A SUBSTRATE

(57) Abstract: This invention concerns a process for coating a substrate, and an extrusion coating structure. According to the present process, the coating is provided by producing a bimodal polyethylene composition by subjecting ethylene, optionally with hydrogen and/or comonomers to polymerization or copolymerization reactions in a multistage polymerization sequence of successive polymerization stages. The polymerization reactions are carried out in the presence of a single site catalyst capable of forming a composition which comprises a low molecular weight component with an MFR₂ of 20 g/10 min or more and a density higher than the density of the composition, and a high molecular weight component, said composition having a melt flow rate MFR₂ of 5 g/ 10 min or more and a density of 915 - 960 kg/m³. The composition is extruded on the substrate as such or by adding 10 wt-% or less, calculated from the total weight of the coating, of high pressure PE-LD by blending into the extrusion composition or by coextrusion.

PROCESS FOR PRODUCING A POLYETHYLENE COATING ON A SUBSTRATE

Background of the Invention

5

Field of the Invention

The present invention concerns a process for coating a substrate by extruding a polyethylene composition thereon. In addition, the present invention concerns an extrusion
10 coating structure.

Description of Related Art

Low density polyethylene (PE-LD) made by a high pressure process (referred to as "high
15 pressure PE-LD") has been used conventionally for extrusion coating. High pressure PE-LD is easy to process, provides adequate moisture barrier and has good sealing properties. The mechanical properties of high pressure PE-LD are, however, not as good as those of other PE grades. This means that a thicker layer of high pressure PE-LD is needed to achieve the mechanical properties required for a coating.

20

Linear low density polyethylene (PE-LLD), medium density polyethylene (PE-MD) or high density polyethylene (PE-HD) materials exhibit better mechanical properties. On the other hand, a PE composition with a higher density is more difficult to extrude, and the neck-in in extrusion is typically increased as the density increases.

25

The problem of the combination of good mechanical properties and good processability has been tried to overcome by blending high pressure PE-LD with other PE grades.

Another solution has been to coextrude HD, MD or LLD polyethylene together with PE-LD.

30

On the whole, it is desirable to try to decrease the total amount of polyethylene in a coated product due to the demands of environmental regulations. In particular, it is of importance to decrease the amount of high pressure PE-LD in a coated product, because the production of high pressure PE-LD in the world is decreasing. The present focus in polyethylene

production is in the low pressure processes, and thus most often the high pressure PE-LD has to be bought and brought to the plant. This increases the costs of the manufacturer of the extrusion coating.

- 5 WO 98/30628 discloses an extrusion coating structure comprising a bimodal ethylene polymer. The ethylene polymer is a blend of at least two different ethylene polymers and it contains 80 – 100 % ethylene repeating units and 20 – 0 % alpha-olefin repeating units. The density of the ethylene polymer is 0.920 – 0.960 kg/m³.
- 10 The ethylene polymer blend can be made in a reactor sequence using a single site or a Ziegler-Natta type catalyst. The catalyst used in the examples is, however, not defined. It is to be noted that in the examples the materials are either blended with 15 % of high pressure PE-LD or coextruded with PE-LD. According to our experiments this would indicate that the material in the examples is produced using Ziegler-Natta catalysts. Nothing is
- 15 mentioned of the advantages of using a single site catalyst, especially of the possibility of extrusion of the composition without blending or coextruding with high pressure PE-LD when using a polyethylene composition produced by single site catalysts.

- WO 96/16119 discloses a polyethylene extrusion composition comprising from 75 wt-% to 20 95 wt-% of at least one ethylene/α-olefin interpolymer composition having a density in the range of 850 kg/m³ – 940 kg/m³ and from 5 to 25 wt-% of high pressure ethylene polymer. The extrusion composition according to the publication has a melt index equal to or greater than 1 g/10 min. It is stated in the publication that the ethylene/α-olefin interpolymer can be prepared in any conventional way, inter al., by polymerizing in a reactor sequence using 25 a homogeneous single site catalyst. The ethylene/α-olefin interpolymers disclosed in the examples are substantially linear ethylene/1-octene copolymer and a homogeneously branched linear ethylene/1-hexene copolymer. None of these materials is bimodal, and the melt flow properties obtained are due to the long-chain branching of the materials. The catalyst most probably used in the examples is called constrained geometry catalyst, but 30 this is not specifically stated. The polymerization conditions are not defined, either.

US 5 674 342 discloses a process for extrusion coating a substrate. The composition used in the coating process consists according to one alternative solely of ethylene polymer having a Dow Rheology Index (DRI) of at least 0.1. The ethylene polymer is, according to

the examples a substantially linear polymer, which is not bimodal. According to the publication it is possible to use either single site catalysts or constrained geometry catalysts in the polymerization. It is stated in the publication that the constrained geometry catalysts are preferably used and that preferably a solution polymerization process is employed. In 5 the examples, however, the used catalyst or process conditions are not indicated.

For the sake of completeness it should be mentioned that cast films (i.e. not extrusion coatings) have been made of substantially linear polymers having a bimodal molecular weight distribution which have been produced by a metallocene catalyst in a two-stage 10 solution process (WO 99/09096). The polymers produced in the different stages were reported to have equal densities. Specifically, the catalyst has the ability to produce long chain branches in the polymer. The processability of the polymer on the film line was reported to be good. However, based on the disclosure it is not possible to ascertain whether the prior polymers would have a good processability on the extrusion coating line, 15 where the line speed ins 100 – 500 m/min, compared to the film line having a line speed of a few meters per minute.

Summary of the Invention

20 It is an aim of the present invention to eliminate the drawbacks of prior art and to provide a novel process for coating a substrate by extrusion by producing such a bimodal extrusion composition of polyethylene, which can be extruded as such or with addition only of small amounts of high pressure PE-LD either by blending or coextrusion.

25 It is a further object of the present invention to provide a novel extrusion coating structure.

These and other objects, together with the advantages thereof over known processes and products, are achieved by the present invention as hereinafter described and claimed.

30 The invention is based on the surprising finding that by polymerizing ethylene in the presence of a single site catalyst in a multireactor sequence can be obtained a polyethylene composition which exhibits improved mechanical properties and can still be extruded on a substrate either as such or by adding 10 wt-% or less of high pressure PE-LD either by blending into the extrusion composition or by coextrusion.

More specifically, the present process is characterized by what is stated in the characterizing part of claim 1.

5 The extrusion coating structure is characterized by what is stated in the characterizing part of claim 15.

A number of considerable advantages is obtained by means of the present invention. The present process enables the production of a composition which can be used in extrusion 10 coating either as such or blended or coextruded with high pressure PE-LD, the amount of PE-LD being 10 wt-% or less of the total mass of the polyethylene coating. When less high pressure PE-LD is needed in the coating, the production of the coating is cheaper.

The coating produced by the present process exhibits better mechanical properties than 15 high pressure PE-LD and, thus, a thinner layer of the coating is needed. This is in accordance with the public demand to use less polyethylene in the coating for environmental reasons. In particular, the tensile strength and tear strength in machine and transverse directions are on a good level and superior to materials intended for similar purposes. Also the optical properties are better than those of conventional materials; the 20 gloss of the coating film is high and the haze is low.

The present extruded coating structure exhibits excellent resistance to environmental stress cracking. Surprisingly the resistance does not decrease as a function of time. In packaging, this is a true benefit since the manufacturers of liquid products need to be certain that their 25 products are packed so as to ensure a delivery of a non-contaminated product to consumers.

Detailed Description of the Invention

30

Definitions

For the purpose of the present invention, "slurry reactor" designates any reactor operating in slurry, in which reactor the polymer forms in particulate form. As examples of suitable

reactors can be mentioned a continuous stirred tank reactor, a batch-wise operating stirred tank reactor or a loop reactor. According to a preferred embodiment the slurry reactor comprises a loop reactor.

5 By "gas phase reactor" is meant any mechanically mixed or fluidized bed reactor. Preferably the gas phase reactor comprises a mechanically agitated fluidized bed reactor with gas velocities of at least 0.2 m/sec.

10 "Reaction zone" or "polymerisation zone" stands for one or several reactors of similar type producing the same type or characteristics of polymer connected in the series.

By "melt flow rate" or abbreviated "MFR" is meant the weight of a polymer extruded through a standard cylindrical die at a standard temperature in a laboratory rheometer carrying a standard piston and load. MFR is a measure of the melt viscosity of a polymer 15 and hence also of its molecular weight. The abbreviation "MFR" is generally provided with a numerical subindex indicating the load of the piston in the test. Thus, e.g., MFR₂ designates a 2.16 kg load. MFR can be determined using, e.g., by one of the following tests: ISO 1133 C4, ASTM D 1238 and DIN 53735.

20 **The Catalyst**

The catalyst used in the polymerization process is a single site catalyst. According to a preferred embodiment, no fresh catalyst is added to the second polymerization stage. The catalyst should produce a bimodal, i.e., rather broad, molecular weight distribution and 25 comonomer distribution. Additionally, the catalyst should be able to produce a molecular weight of at least 150000 – 200000 g/mol in the high molecular weight polymer fraction, so that good mechanical properties are obtained. Some metallocene catalysts, like those based on a bis-(n-butyl cyclopentadienyl)zirconium dichloride complex and disclosed in FI-A-934917 (= WO 95/12622) are not able to produce a high enough molecular weight 30 polyethylene and their usefulness in bimodal polymerization is limited. It has been found that some metallocene catalysts are able to produce a high enough molecular weight. One example of such catalysts is based on another complex disclosed in WO 95/12622, having the general formula



wherein

X₁ and X₂ are either same or different and are selected from a group containing halogen,
5 methyl, benzyl or hydrogen;
Hf is hafnium;
Cp is a cyclopentadienyl group; and
R₁ and R₂ are the same or different and selected from the group of linear and branched
hydrocarbyl groups containing 1 – 10 carbon atoms.

10

Particularly suitable complexes of the kind described above are bis-(n-butyl cyclopentadienyl) hafnium dihalides. Another group of suitable complexes are the siloxy-substituted bridged bis-indenyl zirconium dihalides, which are disclosed in FI-A-960437 (= WO 97/28170).

15

These catalysts are typically supported on a solid carrier, but they may also be used as unsupported. The carrier is typically inorganic, and suitable materials comprise, e.g., silica (preferred), silica-alumina, alumina, magnesium oxide, titanium oxide, zirconium oxide and magnesium silicate (cf. also WO 95/12622). The catalysts are normally used together 20 with an aluminumoxane cocatalyst. Suitable cocatalysts are, e.g., methylaluminumoxane (MAO), tetraisobutylaluminumoxane (TIBAO) and hexaisobutylaluminumoxane (HIBAO). The cocatalyst is preferably supported on the carrier, typically together with the catalyst complex, although the cocatalyst may optionally be fed into the reactor separately.

25 A catalyst based on bis-(n-butyl cyclopentadienyl) hafnium dihalide complex supported on a silica or a silica-alumina carrier together with a methylaluminoxane cocatalyst is suitable to be run in a process including a loop reactor and a gas phase reactor. Especially suitable is a catalyst based on bis-(n-butyl cyclopentadienyl) hafnium dichloride. Both the complex and the cocatalyst are supported on the carrier.

30

The thus obtained catalyst is then fed into the reactor. The catalyst is easy to feed and the polymer settles well in the loop reactor. This makes the loop reactor operation easy.

In the gas phase reactor the catalyst is able to produce a sufficiently high molecular weight material. This is essential to obtain the required processability on the film extrusion line and good mechanical properties of the film.

5 Polymerization Process

To produce the bimodal polyethylene composition used for extrusion coating according to the invention, ethylene is polymerized in the presence of a single site catalyst at elevated temperature and pressure.

10

Polymerization is carried out in a series of polymerization reactors selected from the group of slurry and gas phase reactors. In the following, the reactor system comprises one loop reactor (referred to as "the first reactor") and one gas phase reactor (referred to as "the second reactor"), in that order.

15

However, it should be understood that the reactor system can comprise the reactors in any number and order. It is also possible to conduct the process in two or more gas phase reactors.

20 The high molecular weight portion and the low or medium molecular weight portion of the product can be prepared in any order in the reactors. It is to be understood that "high" and "low" are the components with a "higher" or "lower" molecular weight compared with each other. A separation stage is normally employed between the reactors to prevent the carryover of reactants from the first polymerization stage into the second one. The first
25 stage is typically carried out using an inert reaction medium.

In every polymerization step it is possible to use also comonomers selected from the group of C₃₋₁₈ olefins, preferably C₄₋₁₀ olefins, such as 1-butene, 1-pentene, 1-hexene, 4-methyl-1-pentene, 1-heptene, 1-octene, 1-nonene and 1-decene as well as mixtures thereof and
30 dienes, such as 1,5-hexadiene and 1,9-decadiene.

In addition to the actual polymerization reactors used for producing the bimodal ethylene homo- or copolymer, the polymerization reaction system can also include a number of additional reactors, such as prereactors and postreactors. The prereactors include any

reactor for prepolymerizing the catalyst and for modifying the olefinic feed, if necessary. The postreactors can be used, for example, for blending additional components such as the small amount of high pressure PE-LD to the polymerization product. All reactors of the reactor system are preferably arranged in series (in a cascade).

5

The polymerization steps may be performed in the most convenient order. Thus, it is possible to polymerize the low molecular weight component in the first step of the process and the high molecular weight component in the second step. It is also possible to perform the steps in a reversed order, i.e., to polymerize the high molecular weight component in the first stage 10 and the low molecular weight component in the second stage. If the first stage involves a slurry polymerization, it is preferred to produce the low molecular weight component in that stage to avoid problems due to the solubility of the polymer.

According to the present invention, the bimodal polyethylene composition for use in 15 extrusion coating is preferably produced by

- subjecting ethylene, optionally with hydrogen and/or comonomers to polymerization or copolymerization reactions in a multistage polymerization sequence of successive polymerization stages,
- carrying out the polymerization reactions in the presence of a single site catalyst 20 capable of forming a composition comprising
 - a low molecular weight component with an MFR₂ of 20 g/10 min or more and a density higher than the density of the composition, and
 - a high molecular weight component,
 - said composition having a melt flow rate MFR₂ of 5 g/ 10 min or more and a 25 density of 915 – 960 kg/m³.

According to a preferred embodiment of the invention, the polymerization comprises the 30 steps of

- subjecting ethylene and optionally hydrogen and/or comonomers to a first polymerization or copolymerization reaction in the presence of a single-site catalyst in a first reaction zone or reactor to produce a first polymerization product with an MFR₂ of 20 g/10 min or more;
- recovering the first polymerization product from the first reaction zone;
- feeding the first polymerization product to a second reaction zone or reactor;

- feeding additional ethylene and, optionally, comonomers to the second reaction zone;
- subjecting the additional ethylene and optionally additional monomer(s) and/or hydrogen to a second polymerization reaction in the presence of the single-site catalyst and the first polymerization product to produce a second polymerization product having a MFR₂ of 5 g/10 min or more; and
- recovering the combined polymerization product from the second reaction zone.

In the first step of the process, ethylene with the optional comonomer(s) is fed into the first polymerization reactor. Along with these components is optionally fed also hydrogen, which functions as a molecular weight regulator. The amount of hydrogen depends on the desired molecular weight of the polymer. The catalyst may be fed to the reactor together with the reagents or, preferably, prior to the reagents, normally by flushing with a diluent.

The polymerization medium typically comprises the monomer (i.e. ethylene) and/or a hydrocarbon, in particular, a light inert hydrocarbon, such as propane, iso-butane, n-butane or isopentane. The fluid is either liquid or gaseous. In the case of a slurry reactor, in particular a loop reactor, the fluid is liquid and the suspension of polymer is circulated continuously through the slurry reactor, whereby more suspension of polymer in particle form in a hydrocarbon medium or monomer will be produced.

The conditions of the slurry reactor are selected so that 30 – 70 wt-%, preferably 40 – 60 wt-%, of the whole production is polymerized in the slurry reactor(s). The temperature is in the range of 40 to 110 °C, preferably in the range of 70 to 100 °C. The reaction pressure is in the range of 25 to 100 bar, preferably 35 to 80 bar, and the mole fraction of ethylene in the liquid phase is typically 4 – 10 % by mole. In order to produce a polyethylene having a density in excess of 960 kg/m³, the polymerization is preferably carried out at supercritical conditions at temperatures over 90 °C. In slurry polymerization more than one reactor can be used in series. In such a case the polymer suspension in a reaction medium produced in the slurry reactor is fed without separation of inert components and monomers intermittently or continuously to the following slurry reactor, which acts at lower pressure than the previous slurry reactor.

The polymerization heat is removed by cooling the reactor with a cooling jacket. The residence time in the slurry reactor must be at least 10 minutes, preferably 20-100 min for obtaining a sufficient degree of polymerization.

5 As discussed above, if a low molecular weight polyethylene is the desired product, hydrogen is fed into the reactor. With a catalyst according to the present invention, a very small amount of hydrogen is sufficient to produce a high MFR₂ polyethylene. Thus, an MFR₂ of 50 – 300 g/10 min can be obtained with a hydrogen-to-ethylene feed ratio between 0.1 – 0.5 kg of hydrogen/ton of ethylene. The hydrogen is typically consumed in
10 the reactor, so that the molar ratio of hydrogen to ethylene in the reaction mixture is between 0.4 and 1 kmol, or 400 – 1000 ppm by volume.

After the first reaction zone, the volatile components of the reaction medium are typically evaporated. As a result of the evaporation, hydrogen is removed from the product stream.
15 The stream can be subjected to a second polymerization in the presence of additional ethylene to produce a high molecular weight polymer.

The second reactor is preferably a gas phase reactor, wherein ethylene and preferably comonomers are polymerized in a gaseous reaction medium in the presence of a single-site catalyst. If it is desirable to obtain a high molecular weight polymer, the polymerization is carried out essentially in the absence of hydrogen. The expression "essentially in the absence of hydrogen" means, for the purposes of this invention, that no additional hydrogen is fed to the reactor and the molar ratio of hydrogen to ethylene in the reactor is lower than 0.6 mol/kmol (600 ppm by volume), preferably less than 0.4 mol/kmol (400 ppm by volume). The gas phase reactor can be an ordinary fluidized bed reactor, although other types of gas phase reactors can be used. In a fluidized bed reactor, the bed consists of the formed and growing polymer particles as well as still active catalyst come along with the polymer fraction. The bed is kept in a fluidized state by introducing gaseous components, for instance monomer and optionally comonomer(s) on such a flow rate that will make the particles act as a fluid. The fluidizing gas can contain also inert carrier gases, like nitrogen and propane and also hydrogen as a molecular weight modifier. The fluidized gas phase reactor can be equipped with a mechanical mixer.

The gas phase reactor used can be operated in the temperature range of 50 to 115 °C, preferably between 60 and 110 °C and the reaction pressure between 10 and 40 bar and the partial pressure of ethylene between 1 and 20 bar, preferably 5 – 10 bar.

5 The production split between the high molecular weight polymerization reactor and the low molecular weight polymerization reactor is 30 – 70 : 70 – 30. Preferably, 30 to 70 wt-%, in particular 40 to 60 %, of the ethylene homopolymer or copolymer is produced at conditions providing a polymer constituting the low molecular weight portion of the polymer, and 70 to 30 wt-%, in particular 60 to 40 wt-%, of the ethylene homopolymer or
10 preferably copolymer is produced at conditions providing the high molecular weight portion of the polymer. The density of the low molecular weight portion is preferably 930 – 975 kg/m³ and the density of the final polymer is preferably 915 to 960 kg/m³.

15 The present ethylene polymers and copolymers of ethylene can be blended and optionally compounded with additives and adjuvants conventionally used in the art. Thus, suitable additives include antistatic agents, flame retardants, light and heat stabilizers, pigments, processing aids and carbon black. Fillers such as chalk, talc and mica can also be used.

The Extrusion Coating Composition

20 According to the present invention, the coating of a substrate is carried out by extruding the bimodal polyethylene composition obtained by the polymerization process described above on the substrate.

25 The polyethylene composition comprises, according to the invention, 30 to 70 wt-%, preferably 40 to 60 wt-%, and in particular 45 to 55 wt-% of a high molecular weight portion, and 70 to 30 wt-%, preferably 60 to 40 wt-%, and in particular 55 to 45 wt-% of a low molecular weight portion. The melt flow rate MFR₂ of the composition is typically 5 g/10 min or more, preferably in the range of 5 – 50 g/10 min, and in particular in the range
30 of 10 – 20 g/10 min.

The density of the polymer product is from about 915 kg/m³ to about 960 kg/m³.

The density of the polymer and the density and the melt flow rate of the low molecular weight component correlate preferably as presented in the following:

If the density of the composition is between 940 – 960 kg/m³, the MFR₂ of the low
5 molecular weight component is preferably between 70 – 1000 g/10 min and the density is
higher than 965 kg/m³.

If the density of the composition is in the medium density area, i.e., between 930 – 940
kg/m³, the low molecular weight component preferably has an MFR₂ between 50 - 1000
10 g/10 min and a density between 940 – 975 kg/m³.

If the density of the composition is low, between 915 – 930 kg/m³, the low molecular
weight component preferably has an MFR₂ between 20 – 500 g/10 min and density
between 935 – 965 kg/m³.

15

The Extrusion

The polymer obtained from the polymerization process is fed, typically in the form of
powder or pellets, optionally together with additives, to a extruding device. The extruding
20 device is known as such and any extruding device known in the art may be used.

As already discussed, according to the present invention the film can be extruded without
adding high pressure PE-LD. Thus, by means of the present invention it is possible to
provide a single layer coating consisting essentially of bimodal polyethylene on a
25 substrate. By "single layer coating" is meant that the coating is provided without
coextrusion with some other polymer. Further, "consisting essentially of bimodal
polyethylene" means that no high pressure PE-LD is added to the extrusion coating
composition and that the composition does not contain significant amounts of other
polymers, either.

30

According to a first embodiment of the present invention high pressure PE-LD is added to
the polymerization product obtained from the polymerization process. The polymerization
product and high pressure PE-LD can be blended, e.g., in a postreactor of the
polymerization process (cf. above) or in the extruder.

According to a second embodiment the polymerization product obtained from the process is coextruded with high pressure PE-LD. The coextrusion is known in the art as such and any extruding device suitable for coextrusion may be used.

5

By adding high pressure PE-LD to the composition it is possible to enhance the processability of the extrusion composition. It is to be noted, however, that the polymer composition obtained from the polymerization process described above already has a good processability in extrusion. Therefore, if it is decided to use high pressure PE-LD, the

10 amount can, and should, be kept low. The amount of high pressure PE-LD, calculated as the weight percentage of the high pressure PE-LD in the polyethylene coating, is typically 10 wt-% or less, preferably 0.1 - 8 wt-%, in particular 0.1 - 5 wt-% and most preferably 0.1 - 3 wt-%.

15 The coating is typically extruded on a fiber based substrate material, such as paper or paperboard (cardboard). The substrate can also be a film made of polyester, cellophane, polyamide, polypropylene or oriented polypropylene. The thickness of the film is typically 10 – 80 µm. Further, the substrate can be an aluminium foil, typically of a thickness from 6 µm to 300 µm.

20

The thickness of the coating is typically about 10 – 200 µm, preferably 30 – 100 µm. The coating weight is typically in the range of 10 – 100 g/m², preferably in the range of 20 – 50 g/m². The composition according to the invention can also be run into a film on a cast film line. A 40 µm cast film produced in this way generally exhibits the following features:

25

- haze 10 % or less, preferably 8 % or less, and in particular 5 % or less;
- gloss 70 % or more, preferably 100 % or more, and in particular 120 % or more;
- puncture strength of 900 N/mm or more, preferably 1000 N/mm or more and, in particular, 1200 N/mm or more;

– tensile strength machine/transverse direction 20/20 MPa or more, preferably 22/21

30

MPa or more; and

– tear strength machine/transverse direction 1.0/1.5 MPa or more, preferably 1.6/1.8 MPa or more, and in particular 1.6/2.0 MPa or more.

The environmental stress cracking resistance, ESCR, values of the films extruded from the present composition are typically in the range of 200 – 1000 %, preferably in the range of 400 – 800 % and in particular in the range of 550 – 700 %. What is to be specifically noted is that the percentage increases as the time for exposure increases at least up to 4 weeks.

5

The odour and taste properties, which necessarily are determined after the coating process, are in the same level as those of known materials.

Description of Analytical Methods

10

All the properties under "End product properties" in Table 1 and all film properties in Table 2 are determined from the extruded film. The film is obtained by first coating a substrate and then tearing the coating from the substrate.

15 Odour

Odour is determined from a structure consisting of the test material coated on a polyester film. The coating weight is 40 g/m², coating speed is 100 m/min and the coating is conducted at 315 °C temperature. After the run the coating is removed from the polyester film and cut to A4 size samples. The samples are put to flasks and aged in an oven at 40 °C for 0.5 hours and 1 hour. The test is carried out by two groups of people, each group consisting of four persons. The persons smell the samples and evaluate their odour in scale 0 – 3 (0=odourless).

Taste

25 Taste is determined from a structure consisting of the test material coated on an aluminium film. The coating conditions are similar to those in the odour test. The structure is cut to three 240 mm times 320 mm pieces, which are sealed into bags. Into the bag is poured 150 ml of water and the samples are put into an oven at 40 °C for two hours. The testing is done by two groups, as in the odour test, who taste the water and rank it in scale 0 – 3 (0 = tasteless).

Environmental Stress Cracking Resistance, ESCR

The environmental stress cracking resistance is measured as the elongation % of a 40 µm film after contact with 10 % Igepal liquid at 50 °C for the indicated time period.

Neck-In

The difference between the width of the die and the final coating width.

5 Gloss

Gloss is measured according to ASTM D 2457v.

Haze

Haze is measured according to ASTM 1003.

10

Secant Modulus

Secant modulus at 1 % elongation is obtained from a tensile experiment, performed according to ISO 1184. The specimen is extended along its major axis at a constant speed. A stress-strain curve is thus obtained. The value of the secant modulus is the ratio of stress 15 to strain at 1 % strain on the stress-strain curve.

Strain at Break

Strain at break is also obtained from a tensile experiment. This is the value of the strain at the point where the specimen breaks.

20

Hot Tack

Hot tack is measured by measuring the force which is needed to tear apart a heat sealed structure before the material has been allowed to cool. Sealing is made at different temperatures (temperature is increased by 5 or 10 °C intervals) and the sealing pressure is 25 1.0 N/mm². Sealing is made in 0.2 seconds. Tearing is started after 0.1 seconds from sealing and the tearing rate is 200 mm/s.

Puncture

The puncture test has been carried out according to ASTM D4649.

30

Tensile strength

The experiment is performed according to ISO 1184 method. The specimen is extended along its major axis at a constant speed. Normal 50 mm could be used as a distance between grips (gauge length) in film tensile testing. 125 mm gauge length would be

required for tensile modulus measurement so this was not possible for 100 mm cast film in transverse direction.

Tear strength

5 Tear testing is done according to ASTM 1922. Machine direction is easier, as the thickness variation in critical test direction is better controlled. Thickness varied more in transverse direction and occasionally difficulties arise in taking the sample in a manner which guarantees an even thickness for the critical testing area.

10 WVTR

The water vapour transmission rate is measured in a diffusion cell where above the sample flows a stream of dry air and below the sample is an atmosphere with a constant humidity at a constant temperature (usually 37.8 °C). When the sample has reached an equilibrium, the air stream is directed to an IR detector determining the water content of the air stream.

15 In this way can the water vapour transmission rate be measured. This method gives approximately five times higher WVTR values than ASTM E-96.

The invention is further illustrated with the aid of the following examples.

20 **Example 1 – Catalyst preparation**

168 g of a metallocene complex (bridged siloxy-substituted bis-indenyl zirconium dichloride, according to WO 97/28170) and 9.67 kg of a 30 % MAO solution supplied by Albemarle were combined and 3.18 kg dry, purified toluene was added. The thus obtained 25 complex solution was added on 9 kg silica carrier SP9-243 by Grace having a particle size of 20 microns, pore volume of 1.5 – 1.7 mm³ and specific surface area of 350 – 400 mm²/g. The complex was fed very slowly with uniform spraying during 2 hours. Temperature was kept below 30 °C.

30 The thus obtained catalyst was dried under nitrogen for 6 h at 75 °C temperature. After nitrogen drying, the catalyst was further dried under vacuum for 10 h.

Example 2

Into a continuously operating 500 dm³ loop reactor, operated at 85 °C temperature and 60 bar pressure, were introduced propane diluent, ethylene, 1-butene comonomer and 5 hydrogen together with a single site polymerization catalyst described in Example 1 so that 25 kg/h of ethylene copolymer having an MFR₂ of 90 g/10 min and a density of 936 kg/m³ was produced. The polymer slurry was withdrawn from the reactor, the hydrocarbons were flashed off and the polymer was introduced into the gas phase reactor operated at 75 °C temperature and 20 bar pressure. Additional ethylene and 1-butene comonomer were 10 introduced into the reactor so that the ethylene copolymer having an MFR₂ of 5.6 g/10 min and a density of 924 kg/m³ was withdrawn from the reactor at a rate of 51 kg/h. The polymer was compounded in a corotating intermeshing twin screw extruder and pelletized.

15 The pelletized product was extruded on a substrate. The properties of the extrusion composition and the extruded film are presented in Table 1.

Example 3 (Comparative)

A polyethylene composition of commercial high pressure PE-LD was extruded on a 20 substrate. The properties of the composition and the extruded film are presented in Table 1.

Example 4 (Comparative)

25 Into a continuously operating 500 dm³ loop reactor, operated at 85 °C temperature and 60 bar pressure, were introduced propane diluent, ethylene, 1-butene comonomer and hydrogen together with a Ziegler-Natta polymerization catalyst prepared according to Example 3 of WO 95/35323, so that 25 kg/h of ethylene copolymer having an MFR₂ of 100 g/10 min and a density of 941 kg/m³ was produced. The polymer slurry was withdrawn from the reactor, the hydrocarbons were flashed off and the polymer was 30 introduced into the gas phase reactor operated at 75 °C temperature and 20 bar pressure. Additional ethylene and 1-butene comonomer were introduced into the reactor so that ethylene copolymer having an MFR₂ of 10 g/10 min and a density of 931 kg/m³ was withdrawn from the reactor at a rate of 51 kg/h. The polymer was compounded in a corotating intermeshing twin screw extruder and pelletized.

The pelletized product was extruded on a substrate. The properties of the extrusion composition and the extruded film are presented in Table 1.

5 **Table 1**

	Ex. 2	Ex. 3	Ex. 4
MFR ₂ g/10 min	5.6	7.5	12
Dens. kg/m ³	924	920	932
Film appearance	---	+++	--
Melt T °C	315	315	285
Max rpm	117	> 200	164
Coat. weight variation g/m ² (coex 5 + 5 g/m ² , 200 m/min)	9-11	0	8-10
N-I mm	135	65	114
End product properties			
Odor (1-3) BTM 14137	1.0	1.3	0.9
Taste (1-3) BTM 14138	1.3	1.4	0.7
ESCR, % 0 week 2 weeks 4 weeks	580 600 670	160 10 4	650 750 470
Hot tack N/°C	2.9/115	2.5/105	4.2/120
Mechanicals, 40 µm cast Tens 1% secmod md/cd Mpa Strain a break % Tens.strength md/cd MPa Tear md/cd N Punct. N/mm Haze % Gloss	148/158 740/710 23/21.5 1.68/2.48 1215 3.4 126	130/135 500/620 18/17 1.60/1.71 1105 6.8 83	227/236 920/970 21/20 0.94/0.94 853 16.7 105
WVTR [*] g/m ² *24h	13.9	13.5 ^{**}	13.3

^{*} Co-ex 10 gsm high pressure PE-LD of Ex. 3 + 20 gsm test material; RH 90%; T 38°C

^{**} LE4524 30 gsm mono

The processability of the coating composition according to the present invention is on the same level as for the bimodal polyethylene produced in the presence of a Ziegler-Natta catalyst. The processability of high pressure PE-LD is, as expected, slightly better.

ESCR of both bimodal materials is superior to that of high pressure PE-LD. The composition according to the present invention has a superior time behaviour compared with the bimodal Ziegler-Natta material.

5 Secant modulus is a function of the density of the material, which is also verified by the values shown in Table 1. The same seems to apply for strain at break.

The material according to the present invention exhibits higher tensile and tear strengths both in machine and transverse directions than either of the two other materials. Also the
10 puncture strength of the material produced according to the present invention is higher than those of the reference materials.

The optical properties, haze and gloss, are better than those of the other two materials.

15 The differences in initial sealing temperatures (hot tack) are probably due to differences in density.

Example 5 - Coextrusion tests

20 The sample 'Single site catalyst' is a sample produced by polymerizing ethylene and 1-butene comonomer in two cascaded gas phase reactors in the presence of a catalyst prepared according to WO 95/12622, comprising a bis-(n-butylcyclopentadienyl)zirconium dichloride complex and MAO on a silica carrier. After the first reactor the MFR₂ of the polymer was 100 g/10 min and the density was 945 kg/m³. The final polymer had an MFR₂
25 of 6 g/10 min and a density of 935 kg/m³. The production split was 50/50.

The sample has been run on a Beloit line in coextrusion, with 15 g/m² PE-LD and 15 g/m² the sample of the material according to the invention. Thus, the amount of PE-LD is not in accordance with the present invention, but the aim of this example is to compare the
30 properties of a material produced with a single site catalyst and a material produced with a Ziegler-Natta catalyst. A reference run was made using 30 g/m² PE-LD only. The physical properties of the coated paper were determined from both runs.

The sample 'Ziegler-Natta' is a sample produced using a Ziegler-Natta catalyst according to Example 3 of WO 98/30628. The sample has MFR₂ = 9 and density = 931 kg/m³.

5 The sample has been run on a Beloit line in coextrusion, with 5 g/m² PE-LD and 15 g/m² of the Ziegler-Natta material. A reference run was made using 20 g/m² PE-LD only. The physical properties of the coated paper were determined from both runs.

10 Since the coating weights of the SSC and Z-N materials have been different, a direct comparison of the values of the mechanical properties would not be feasible. Instead, the figures of both materials were compared to a reference run made with the same coating weight using PE-LD. The values of tensile strength, elongation, tear strength and burst force indicate what is the value of the property of the linear coextruded coating compared to the PE-LD reference. Thus, a figure 190 % indicates, that the property has been improved by 90 % compared to PE-LD.

15 Table 2 indicates, that with respect to tensile strength and elongation, both materials give a similar improvement compared to the PE-LD. With respect to tear strength and burst force, the SSC material seems to give a bigger improvement.

20 The hot tack and cold tack values are similar, measured from similar samples. The results indicate that the Ziegler-Natta material gives a slightly higher force, but the single site material gives a lower temperature. The latter result is even more positive when considering the higher density of the single site catalyst material sample (935 kg/m³ vs. 931 kg/m³).

Table 2

		Ziegler-Natta	Single site catalyst
MFR ₂	g/10 min	9	6
Density	kg/m ³	931	935
Tensile strength	MD	83 %	109 %
	TD	143 %	149 %
Elongation	MD	190 %	204 %
	TD	164 %	136 %
Tear strength	MD	107 %	145 %
	TD	109 %	162 %
Burst force		176 %	210 %
Hot tack	Force, N	3.9	3.2
	Temp., °C	120	115
Cold tack	Force, N	8.5	6.2
	Temp., °C	125	115
WVTR	g/m ² /24 h		13.5

Claims:

1. Process for coating a substrate, comprising
 - producing a bimodal polyethylene composition by
 - 5 – subjecting ethylene, optionally with hydrogen and/or comonomers to polymerization or copolymerization reactions in a multistage polymerization sequence of successive polymerization stages;
 - carrying out the polymerization reactions in the presence of a single site catalyst capable of forming a composition comprising
 - 10 – a low molecular weight component with an MFR₂ of 20 g/10 min or more and a density higher than the density of the composition, and
 - a high molecular weight component, said composition having a melt flow rate MFR₂ of 5 g/ 10 min or more and a density of 915 – 960 kg/m³; and
 - 15 – extruding said composition on the substrate as such or by adding 10 wt-% or less, calculated from the total weight of the coating, of high pressure PE-LD by blending into the extrusion composition or by coextrusion.
2. The process according to claim 1, wherein the bimodal polyethylene composition is produced by
 - subjecting ethylene, optionally with hydrogen and/or comonomers to a first polymerization or copolymerization reaction in the presence of a single-site catalyst in a first reaction zone or reactor to produce a first polymerization product with an MFR₂ of 20 g/10 min or more;
 - 25 – recovering the first polymerization product from the first reaction zone;
 - feeding the first polymerization product to a second reaction zone or reactor;
 - feeding additional ethylene and, optionally, comonomers to the second reaction zone;
 - subjecting the additional ethylene and optionally additional monomer(s) and/or hydrogen to a second polymerization reaction in the presence of the single-site catalyst and the first polymerization product to produce a second polymerization product having a MFR₂ of 5 g/10 min or more; and
 - 30 – recovering the combined polymerization product from the second reaction zone.

3. The process according to claim 1 or 2, wherein 0.1 – 8 wt-%, preferably 0.1 – 5 wt-% and in particular 0.1 – 3 wt-%, calculated from the total weight of the coating composition, of high pressure PE-LD is blended into the polyethylene composition prior to the
5 extrusion.
4. The process according to claim 1 or 2, wherein the composition is coextruded on the substrate together with high pressure PE-LD so as to form a coating comprising 0.1 – 8 wt-%, preferably 0.1 – 5 wt-%, and in particular 0.1 – 3 wt-%, calculated from the total weight
10 of the coating, of high pressure PE-LD.
5. The process according to any of the preceding claims, wherein a metallocene catalyst is used as the single site catalyst.
- 15 6. The process according to any of the preceding claims, wherein the MFR₂ of the low molecular weight component is 50 g/10 min or more, preferably 70 g/10 min or more.
7. The process according to any of the preceding claims, wherein the substrate is paper or paperboard.
20
8. The process according to any of the preceding claims, wherein the active complex of the catalyst has the general formula

(X₁)(X₂)Hf(Cp-R₁)(Cp-R₂),

25

wherein

X₁ and X₂ are the same or different and selected from the group comprising halogen, methyl, benzyl and hydrogen;

Hf is hafnium;

30 Cp is a cyclopentadienyl group; and

R₁ and R₂ are the same or different and stand for linear and branched hydrocarbyl groups containing 1 – 10 carbon atoms.

9. The process according to claim 8, wherein the active complex of the catalyst is bis-(n-butyl cyclopentadienyl) hafnium dihalide.
10. The process according to any of claims 1 – 7, wherein the active complex of the catalyst is a siloxy-substituted bis-indenyl zirconium dihalide.
11. The process according to any of the preceding claims, wherein essentially no fresh catalyst is added to the reactors other than the first one.
- 10 12. The process according to any of the preceding claims, wherein 30 to 70 %, in particular 40 to 60 %, of the ethylene homopolymer or copolymer is produced at conditions which provide a polymer having a MFR₂ of 10 g/10 min or more and 70 to 30 %, in particular 60 to 40 %, of the ethylene homopolymer or copolymer is produced at conditions which provide a polymer having a MFR₂ of less than 5 g/10 min.
- 15 13. The process according to any of claims 1 – 12, wherein the process is carried out in a polymerization reactor cascade comprising a loop reactor and a gas phase reactor, in that order.
- 20 14. The process according to any of claims 1 – 12, wherein the process is carried out in a polymerization reactor cascade comprising two or more gas phase reactors.
15. An extrusion coating structure provided on a substrate comprising at least one layer of bimodal polyethylene composition, characterized in that the composition is produced by
 - subjecting ethylene, optionally with hydrogen and/or comonomers to polymerization or copolymerization reactions in a multistage polymerization sequence of successive polymerization stages;
 - carrying out the polymerization reactions in the presence of a single-site catalyst capable of forming a composition comprising
 - a low molecular weight component with an MFR₂ of 20 g/10 min or more and a density higher than the density of the composition, and
 - a high molecular weight component,
- 25
- 30

said composition having a melt flow rate MFR_2 of 5 g/10 min or more and a density of 915 – 960 kg/m³;

said layer of bimodal polyethylene composition exhibiting

- 5 – tensile strength machine/transverse direction of 20/20 MPa or more,
- tear strength machine/transverse direction of 1.0/1.5 MPa or more, and
- puncture strength of 900 N/mm or more, preferably 1000 N/mm or more.

16. The coating structure according to claim 15, characterized in that the layer of bimodal polyethylene composition further exhibits haze of 10 % or less.

10

17. The coating structure according to claim 15, characterized in that the layer of bimodal polyethylene composition further exhibits gloss of 70 % or more.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI 01/00161

A. CLASSIFICATION OF SUBJECT MATTER

IPC7: C08L 23/04, C08F 10/02, C08F 297/08, B29C 47/02
 According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC7: C08L, C08F, B29C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6025448 A (ROBERT D. SWINDOLL ET AL), 15 February 2000 (15.02.00), column 1, line 66 - column 2, line 4; column 2, line 58 - column 3, line 6; column 4, line 18 - line 52, column 5, line 19 - line 24, column 6, line 11 - line 12, table 1, abstract --	1-17
X	WO 9909096 A1 (THE DOW CHEMICAL COMPANY), 25 February 1999 (25.02.99), page 1; page 3, line 19 - page 4, line 29, claims 1,6,19, abstract --	1-17
A	US 5674342 A (TODD J. OBIJESKI ET AL), 7 October 1997 (07.10.97), claims, abstract --	1-17

 Further documents are listed in the continuation of Box C. See patent family annex.

* Special categories of cited documents	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	"X"	document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E" earlier application or patent but published on or after the international filing date	"Y"	document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&"	document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means		
"P" document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search	Date of mailing of the international search report
27 June 2001	28-06-2001
Name and mailing address of the ISA/ Swedish Patent Office Box 5055, S-102 42 STOCKHOLM Facsimile No. + 46 8 666 02 86	Authorized officer Monika Bohlin/ELY Telephone No. + 46 8 782 25 00

INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI 01/00161

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5047468 A (KIU H. LEE ET AL), 10 Sept 1991 (10.09.91), column 1, line 42 - line 49, claims, abstract, table --	1-17
A	WO 9703139 A1 (BOREALIS POLYMERS OY), 30 January 1997 (30.01.97), abstract --	1-17
P,A	US 6127484 A (LEONARD V. CRIBBS ET AL), 3 October 2000 (03.10.00), column 2, line 15 - line 67, abstract -- -----	1-17

INTERNATIONAL SEARCH REPORT

Information on patent family members

28/05/01

International application No.

PCT/FI 01/00161

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 6025448 A	15/02/00	US 5844045 A	01/12/98
		US 5869575 A	09/02/99
		AT 156827 T	15/08/97
		AU 645519 B	20/01/94
		AU 6203990 A	07/03/91
		BR 9004460 A	10/09/91
		CA 2024333 A	01/03/91
		CN 1029850 B	27/09/95
		CN 1049849 A	13/03/91
		CZ 287632 B	17/01/01
		CZ 9902974 A	11/10/00
		DE 774468 T	02/06/99
		DE 69031255 D,T	05/03/98
		EP 0416815 A,B	13/03/91
		SE 0416815 T3	
		EP 0764653 A	26/03/97
		EP 0764654 A	26/03/97
		EP 0764664 A	26/03/97
		EP 0765888 A	02/04/97
		EP 0774468 A	21/05/97
		ES 2106020 T	01/11/97
		FI 904276 D	00/00/00
		HK 1001918 A	00/00/00
		HU 209316 B	28/04/94
		HU 905704 D	00/00/00
		IL 95542 D	00/00/00
		JP 2535249 B	18/09/96
		JP 2623070 B	25/06/97
		JP 2684154 B	03/12/97
		JP 3163088 A	15/07/91
		JP 7053618 A	28/02/95
		JP 7070223 A	14/03/95
		KR 181710 B	15/05/99
		KR 191226 B	15/06/99
		KR 191380 B	15/06/99
		NO 176964 B,C	20/03/95
		NO 179043 B,C	15/04/96
		NO 301376 B	20/10/97
		NO 309002 B	27/11/00
		NO 903797 D	00/00/00
		NO 933289 D	00/00/00
		NO 933290 D	00/00/00
		NO 954469 A	01/03/91
		NZ 235032 A	28/04/93
		PL 166689 B	30/06/95
		US 5703187 A	30/12/97
		US 5872201 A	16/02/99
		US 6013819 A	11/01/00
		US 6075077 A	13/06/00
		US 6087447 A	11/07/00
		US 6107374 A	22/08/00
		RU 2073018 C	10/02/97
		ZA 9006969 A	27/05/92
		US 5763547 A	09/06/98

INTERNATIONAL SEARCH REPORT

Information on patent family members

28/05/01

International application No.

PCT/FI 01/00161

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9909096 A1	25/02/99	AU 8480898 A BR 9811608 A CN 1267315 T EP 1003812 A NO 20000723 A TR 200000397 T	08/03/99 05/09/00 20/09/00 31/05/00 14/02/00 00/00/00

INTERNATIONAL SEARCH REPORT
Information on patent family members

28/05/01

International application No.

PCT/FI 01/00161

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5674342 A	07/10/97	AT 182511 T	15/08/99
		CA 2165191 A	12/01/95
		DE 69419757 D,T	18/11/99
		EP 0706448 A,B	17/04/96
		SE 0706448 T3	
		ES 2135591 T	01/11/99
		FI 956302 A	28/12/95
		JP 8512002 T	17/12/96
		US 5395471 A	07/03/95
		US 5582923 A	10/12/96
		US 5773155 A	30/06/98
		US 5863665 A	26/01/99
		WO 9501250 A	12/01/95
		CA 2120766 A	29/04/93
		DE 9219090 U	25/09/97
		DE 9219173 U	25/03/99
		DE 69220077 D,T	20/11/97
		DE 69228265 D,T	02/06/99
		EP 0608369 A,B	03/08/94
		SE 0608369 T3	
		EP 0783006 A,B	09/07/97
		SE 0783006 T3	
		EP 0899278 A	03/03/99
		EP 0899279 A	03/03/99
		ES 2103976 T	01/10/97
		ES 2127030 T	01/04/99
		FI 941727 A	31/05/94
		JP 2963199 B	12/10/99
		JP 7500622 T	19/01/95
		KR 262024 B	15/07/00
		US 5272236 A	21/12/93
		US 5278272 A	11/01/94
		US 5380810 A	10/01/95
		US 5427807 A	27/06/95
		US 5525695 A	11/06/96
		US 5562958 A	08/10/96
		US 5591390 A	07/01/97
		US 5595705 A	21/01/97
		US 5665800 A	09/09/97
		US 5677383 A	14/10/97
		US 5685128 A	11/11/97
		US 5783638 A	21/07/98
		US 5847053 A	08/12/98
		US 5852152 A	22/12/98
		US 5972444 A	26/10/99
		US 5986028 A	16/11/99
		US 6060567 A	09/05/00
		US 6111023 A	29/08/00
		US 6136937 A	24/10/00
		US 6140442 A	31/10/00
		US 6194532 B	27/02/01
		WO 9308221 A	29/04/93
		CA 2145644 A	28/04/94
		EP 0665863 A	09/08/95
		FI 951799 A	13/04/95

INTERNATIONAL SEARCH REPORT

Information on patent family members

28/05/01

International application No.

PCT/FI 01/00161

Patent document cited in search report		Publication date	Patent family member(s)		Publication date	
US	5674342	A	07/10/97	JP MX WO	8502532 T 9306405 A 9409060 A	19/03/96 31/05/94 28/04/94
<hr/>						
US	5047468	A	10/09/91	AT AU AU BR CA CN CN CZ CZ DE EG EP SE ES FI GR HU HU HU JP JP JP JP KR NO NO NZ PH PL PT SK SK TR US US ZA	138087 T 619357 B 4469989 A 8905803 A 2002992 A,C 1040219 B 1043721 A 282728 B 8906463 A 68926490 D,T 18942 A 0369436 A,B 0369436 T3 2087067 T 895432 D 3019960 T 53380 A 206508 B 895915 D 2087598 C 2199106 A 7116256 B 9500037 B 173242 B,C 894548 A 231393 A 26989 A 163483 B 92322 A,B 280092 B 646389 A 24887 A 5126398 A 5149738 A 8908724 A	15/06/96 23/01/92 24/05/90 12/06/90 16/05/90 14/10/98 11/07/90 17/09/97 11/06/97 02/10/96 30/06/94 23/05/90 16/07/96 00/00/00 31/08/96 28/10/90 30/11/92 00/00/00 02/09/96 07/08/90 13/12/95 07/01/95 09/08/93 18/05/90 26/02/91 28/12/92 29/04/94 31/05/90 06/08/99 06/08/99 20/07/92 30/06/92 22/09/92 29/08/90
<hr/>						

INTERNATIONAL SEARCH REPORT

Information on patent family members

28/05/01

International application No.

PCT/FI 01/00161

Patent document cited in search report	Publication date		Patent family member(s)	Publication date
WO 9703139 A1	30/01/97		AU 3034997 A	07/01/98
			AU 6308096 A	10/02/97
			BR 9609604 A	25/05/99
			CA 2226549 A	30/01/97
			CN 1195363 A	07/10/98
			EP 0837915 A	29/04/98
			EP 0902809 A	24/03/99
			FI 962366 A	08/12/97
			PL 325016 A	06/07/98
			WO 9747682 A	18/12/97
			AU 693784 B	09/07/98
			AU 6374896 A	10/02/97
			BR 9609621 A	06/04/99
			CA 2225858 A	30/01/97
			CN 1190417 A	12/08/98
			CZ 9800065 A	15/04/98
			DE 69604296 D,T	06/04/00
			EP 0837905 A,B	29/04/98
			ES 2138357 T	01/01/00
			HU 218740 B	28/11/00
			HU 9802544 A	29/03/99
			JP 3088467 B	18/09/00
			JP 10511734 T	10/11/98
			PL 324435 A	25/05/98
			RU 2137788 C	20/09/99
			SE 504455 C	17/02/97
			SE 9502508 A	11/01/97
			TW 411353 B	00/00/00
			WO 9703124 A	30/01/97
			ZA 9605857 A	27/01/97
US 6127484 A	03/10/00		NONE	